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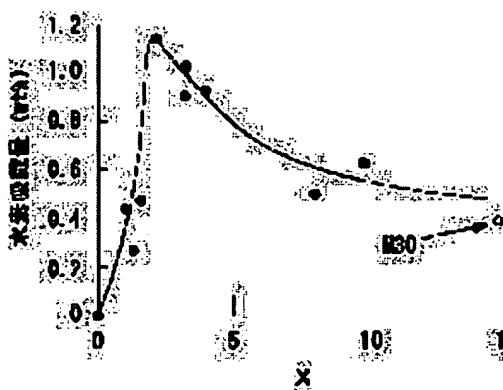
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(54) HYDROGEN GAS OCCLUDING SUBSTANCE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrogen gas occluding substance which has a large quantity of hydrogen occlusion and enables easily storing hydrogen gas near room temperature.

SOLUTION: This hydrogen gas occluding substance comprises a reaction product of alkali metal and carbon material. When the carbon material is amorphous, the molar ratio of amorphous carbon to alkali metal is preferably ≥ 1.3 and ≤ 26 . Further, when the carbon material is graphite, the mole ratio of the graphite to alkali metal is preferably ≥ 2.7 and < 8 .



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CLAIMS

[Claim(s)]

[Claim 1] The hydrogen gas occluded substance with which it consists of a reactant of amorphous carbon and alkali metal, and the mole ratio of said amorphous carbon to said alkali metal is characterized by or more 1.3 being 26 or less.

[Claim 2] Said amorphous carbon is what was obtained by heat-treating one sort or two sorts or more of ingredients chosen from the raw coke obtained from a high molecular compound, naturally-occurring polymers and petroleum, or coal at the temperature of 500 degrees C or more, activated carbon, or a hydrogen gas occluded substance according to claim 1 which is any one or more [of a carbon fiber].

[Claim 3] The hydrogen gas occluded substance with which it consists of a reactant of a graphite and alkali metal, and the mole ratio of said graphite to said alkali metal is characterized by or more 2.7 being less than eight.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the hydrogen gas occluded substance which consists of a reactant of carbon materials, such as amorphous carbon and a graphite, and alkali metal in more detail about a hydrogen gas occluded substance.

[0002]

[Description of the Prior Art] A graphite crystal incorporates the chemical species (INTAKARANTO) of the atom of varieties, a molecule, ion, etc. between layers, and making an intercalation compound is known. The periodicity (stage structure) of the INTAKARANTO layer to a graphite layer and the structure in an INTAKARANTO layer change with INTAKARANTO or the synthetic conditions to be used a lot, and a graphite lamellar compound has the description that a completely different compound of an

appearance and a property is obtained.

[0003] Especially the graphite lamellar compound that incorporated alkali metal as INTAKARANTO shows the property to emit hydrogen and to return to the original alkali-metal-graphite lamellar compound, when the 3 yuan intercalation compound which generated the 3 yuan intercalation compound of alkali-metal-graphite-hydrogen and was generated when it was made to react with hydrogen under specific conditions is heated to predetermined temperature. Therefore, as for the alkali-metal-graphite lamellar compound, the application to a hydrogen gas storage means or a hydrogen gas concentration means is expected.

[0004] As an alkali-metal-graphite lamellar compound in which a hydrogen gas occlusion operation is shown, KC8, RbC8, KC24, RbC24, and CsC24 grade are known. Among these, KC8 and RbC8 are the compounds of the high temperature form which carries out occlusion of the hydrogen near a room temperature, and they form the 3 yuan intercalation compound expressed with the presentation of $\text{KC8H}_{2/3}$, and $\text{RbC8H}_{0.05}$ by adsorbing hydrogen, respectively. On the other hand, KC24, RbC24, and CsC24 are the compounds of the low temperature form which carries out occlusion of the hydrogen near liquid nitrogen temperature, and form the 3 yuan intercalation compound expressed with the presentation of KC24H_4 , RbC24H_4 , and CsC24H_4 by physisorbing hydrogen, respectively.

[0005]

[Problem(s) to be Solved by the Invention] Since the alkali-metal-graphite lamellar compound of the high temperature form represented by KC8 and RbC8 can perform occlusion of hydrogen near the room temperature, it has the advantage that handling is easy. However, the hydrogen storage capacity (weight of the occlusion hydrogen to the weight of a 3 yuan intercalation compound comparatively) of KC8 and RbC8 is 0.50wt% and 0.028wt(s)%, and has the problem that there are few hydrogen storage capacities, as compared with the hydrogen storing metal alloy represented by LaNi_5 , respectively.

[0006] On the other hand, the alkali-metal-graphite lamellar compound of the low temperature form represented by KC24, RbC24, and CsC24 has the advantage that there are many hydrogen storage capacities, as compared with the alkali-metal-graphite lamellar compound of a high temperature form. Especially the hydrogen storage capacity of KC24 has a value almost equivalent to a hydrogen storing metal alloy. However, since the alkali-metal-graphite lamellar compound of a low temperature form must perform occlusion of hydrogen near liquid nitrogen temperature, practicality has the fault of being scarce.

[0007] The technical problem which this invention tends to solve has many hydrogen storage capacities, and they are to offer the hydrogen gas occluded substance which can store hydrogen easily near a room temperature moreover.

[0008]

[Means for Solving the Problem] The hydrogen gas occluded substance applied to this invention in order to solve the above-mentioned technical problem consists of a reactant of amorphous carbon and alkali metal, and the mole ratio of said amorphous carbon to said alkali metal makes it a summary to or more 1.3 be 26 or less.

[0009] If amorphous carbon and alkali metal are made to react, the reactant by which some alkali metal [at least] was doped by amorphous carbon will be obtained. If this is contacted in hydrogen in a room temperature, occlusion of the hydrogen gas will be

carried out also not only between the front face of amorphous carbon but between the clearance between the microcrystals which constitute amorphous carbon, or the layer of microcrystal. Therefore, a hydrogen storage capacity increases as compared with an amorphous carbon independent case.

[0010] Moreover, the 2nd hydrogen gas occluded substance concerning this invention consists of a reactant of a graphite and alkali metal, and the mole ratio of said graphite to said alkali metal makes it a summary to or more 2.7 be less than eight.

[0011] If a graphite and alkali metal are made to react so that the mole ratio of a graphite to alkali metal may become less than [2.7 or more] eight, the mixture which consists of an alkali-metal-graphite lamellar compound of a high temperature form and a superfluous alkali metal will be obtained. If this is contacted in hydrogen in a room temperature, hydrogen gas will enter between the layers of a graphite with a superfluous alkali metal, and will form the intercalation compound of 3 yuan. Therefore, a hydrogen storage capacity increases as compared with the alkali-metal-graphite lamellar compound of the high temperature form known conventionally.

[0012]

[Embodiment of the Invention] Hereafter, the gestalt of 1 operation of this invention is explained to a detail. The hydrogen gas occluded substance concerning this invention consists of a reactant of a carbon material and alkali metal, and the presentation can be expressed with an empirical formula MC_x . However, among an empirical formula, "M" and "C" express alkali metal and a carbon material, respectively, and "x" expresses the mole ratio of a carbon material C to alkali-metal M.

[0013] Here, although especially alkali-metal M is not limited, one sort or two sorts or more of its elements chosen from Li, Na, K, Rb, and Cs are desirable. Moreover, the all do not need to react with a carbon material and a part of such alkali-metal M [at least] has just reacted with the carbon material.

[0014] Any of amorphous carbon or a graphite may be used for a carbon material C, and it is not especially limited to it. However, when using amorphous carbon as a carbon material C, as for a mole ratio x, 26 or less [1.3 or more] are desirable. If a mole ratio x becomes less than 1.3 when a carbon material C is amorphous carbon, since the rate of the alkali metal which is not contributed to hydrogen absorption will increase and a hydrogen storage capacity will be reduced, it is not desirable. Moreover, if a mole ratio x exceeds 26, since the rate of the reactant of the alkali metal in which high hydrogen absorption ability is shown, and amorphous carbon will decrease and a hydrogen storage capacity will be reduced, it is not desirable.

[0015] Moreover, it is desirable to use what was obtained by heat-treating one sort or two sorts or more of ingredients specifically chosen from the corks obtained from a high molecular compound, naturally-occurring polymers and petroleum, or coal as amorphous carbon at the temperature of 500 degrees C or more. In this case, it is desirable to perform heat treatment under an inert atmosphere. Moreover, activated carbon, a carbon fiber, etc. may be used for amorphous carbon. Furthermore, these ingredients may be independently used for amorphous carbon, or may be used for it or more combining two of sorts of these.

[0016] On the other hand, when using a graphite as a carbon material C, as for a mole ratio x, less than [2.7 or more] eight are desirable. If a mole ratio x becomes less than 2.7, since the rate of the alkali metal which is not contributed to hydrogen absorption will

increase and a hydrogen storage capacity will be reduced, it is not desirable. Moreover, if a mole ratio x becomes eight or more, since the rate of the alkali-metal-graphite lamellar compound of a high temperature form which shows a hydrogen absorption operation will decrease and a hydrogen storage capacity will fall, it is not desirable.

[0017] Next, an operation of the hydrogen gas occluded substance concerning this invention is explained. Although the hydrogen gas occluded substance concerning this invention consists of a reactant of alkali metal and a carbon material, it shows hydrogen absorption ability higher than the alkali-metal-graphite lamellar compound of the high temperature form known conventionally.

[0018] For example, originally the amorphous carbon itself represented by activated carbon has the operation which makes hydrogen gas adsorb [near the room temperature]. In this case, hydrogen gas is adsorbed in the pore mainly formed in the front face or front face of amorphous carbon. However, as compared with an amorphous carbon independent case, as for the reactant which this amorphous carbon and alkali metal are made to react, and is obtained, a hydrogen storage capacity increases sharply.

[0019] Although some alkali metal [at least] is doped by amorphous carbon by the reaction, this acts as a catalyst at the time of the doped alkali metal being hydrogen absorption, and is considered because occlusion of the hydrogen gas is carried out also not only between the front face of amorphous carbon but between the clearance between the microcrystals of amorphous carbon, or the layer of microcrystal.

[0020] Moreover, as an alkali-metal-graphite lamellar compound in which the operation which carries out occlusion of the hydrogen [near the room temperature] is shown, the graphite lamellar compound of the high temperature form expressed with an empirical formula MC_8 is known. Therefore, if a graphite and alkali metal are made to react so that the mole ratio of a graphite to alkali metal may become less than [2.7 or more] eight when using a graphite as a carbon material, the mixture which consists of a graphite lamellar compound of the high temperature form known conventionally and a superfluous alkali metal will be obtained.

[0021] However, if such a reactant and hydrogen are made to react, the hydrogen storage capacity will increase more than the hydrogen storage capacity expected from the amount of the high temperature form graphite lamellar compound contained in a reactant. A superfluous alkali metal will be incorporated between the layers of a graphite with hydrogen, and this will be considered for the 3 yuan graphite lamellar compound of the alkali-metal-graphite-hydrogen which has a new presentation to generate, if the mixture and hydrogen which consist of a high temperature form graphite lamellar compound and a superfluous alkali metal are contacted.

[0022] Next, the manufacture approach of the hydrogen gas occluded substance concerning this invention is explained. The hydrogen gas occluded substance concerning this invention can be manufactured by various approaches. For example, after mixing alkali metal and a carbon material and carrying out vacuum enclosure of this at a suitable well-closed container, it can manufacture by the approach of carrying out predetermined time heating to predetermined temperature. Moreover, for example, alkali-metal powder and a carbon material can be paid to a ball mill, and it can manufacture also by the mechanical alloying method which carries out forcible churning.

[0023]

[Example] (Example 1) Using activated carbon (M30, Product made from Osaka Gas

chemical), and K as a carbon material and an alkali metal, the mole ratio x of activated carbon to K carried out weighing capacity, respectively so that it might be set to 0, 1.09, 1.33, 1.63, 2.17, 3.26, 4, 8, and 9.77, and it mixed these all over the argon permutation dry box (dew-point: -80 degrees C), respectively.

[0024] Next, these were put into sample cel tubing made from stainless steel (Made in the Suzuki Trading house, outer diameter of 6.35mm), respectively, and after attaching and enclosing joint with the edge of sample cel tubing, it took out from the argon permutation dry box. Similarly, sample cel tubing which enclosed only activated carbon was also prepared.

[0025] Next, joint was removed, after connecting sample cel tubing to the automatic PTC property measuring device (Made in the Suzuki Trading house) and carrying out vacuum suction of the interior of sample cel tubing to 0.13Pa through joint. Then, sample cel tubing was left at 300 degrees C in the electric furnace for 22 hours, and the reactant of K and activated carbon was obtained.

[0026] About the obtained reactant, X diffraction measurement was performed, respectively. Consequently, when it was $x < 8$, it turned out that a reactant is the mixture of the activated carbon with which K and K were doped. Moreover, when it was $x \geq 8$, it turned out that a reactant consists only of activated carbon with which K was doped. In an X diffraction pattern, since small angle scattering peculiar to activated carbon was not seen, K is considered to fill up in the pore on the front face of activated carbon.

[0027] Next, sample cel tubing with which the reactant was enclosed was attached in the automatic PTC property measuring device, and occlusion of the hydrogen was carried out under the conditions of hydrogen pressure 4.95MPa in the room temperature. The mole ratio x of the reactant (this is hereafter called "hydrogen absorption object".) to which occlusion of the hydrogen was carried out, and relation with a hydrogen storage capacity are shown in drawing 1. In addition, the hydrogen storage capacity of activated carbon (M30) was also collectively shown in drawing 1. Drawing 1 shows that the mole ratio x of the hydrogen storage capacity of a hydrogen absorption object is more than $KC8H2/3$ known from the former within the limits of $1.3 \leq x \leq 26$.

[0028] Moreover, X diffraction measurement was performed about the obtained hydrogen absorption object, respectively. Consequently, even if it was the field of $x < 8$ which added K superfluously, peaks, such as KH, were not observed but only the broadcloth diffraction peak resulting from a hydrogen absorption object was observed. Moreover, when the peak of hydrogen desorption was measured with the inert gas conveyance heating-thermal conductivity method, the hydrogen absorption objects obtained by this example to KH being 540 degrees C were 400 degrees C and 900 degrees C.

[0029] The above result will be considered that it is shown that superfluous K enters the interior of activated carbon (for example, between the clearance between microcrystals and the layer of microcrystal etc.) with hydrogen if the reactant and hydrogen gas containing superfluous K are contacted.

[0030] (Example 2) according to the same procedure as an example 1, the reactant of K and graphitized carbon was obtained except the mole ratio x of graphitized carbon to K having carried out weighing capacity, respectively, using graphitized carbon (MCMB 25-28) and K as a carbon material and an alkali metal, so that only graphitized carbon namely, -- might become 0, 1.09, 2.17, 3.26, 4, 5.43, 7.89, 8, 13.02, and infinity.

[0031] X diffraction measurement was performed about the obtained reactant. Consequently, when it was $x < 8$, it turned out that a reactant is the mixture of K and the graphite lamellar compound KC8 of a high temperature form. On the other hand, in the case of $x \geq 8$, it turned out that they are a graphite lamellar compound KC8 and the mixture of graphitized carbon. Furthermore, when differential heat scan analysis was performed about the reactant which is $x < 8$, the exothermic peak corresponding to fusion of a potassium was observed near 60 degree C.

[0032] Next, sample cel tubing with which the reactant was enclosed was attached in the automatic PTC property measuring device, and occlusion of the hydrogen was carried out under the conditions of hydrogen pressure 4.95MPa in the room temperature. The mole ratio x of the obtained hydrogen absorption object and relation with a hydrogen storage capacity are shown in drawing 2 $R > 2$. In addition, the hydrogen storage capacity of graphitized carbon (MCMB 25-28) was also collectively shown in drawing 2. Drawing 2 shows that the mole ratio x of the hydrogen storage capacity of a hydrogen absorption object is more than KC8H_{2/3} known from the former within the limits of $2.7 \leq x < 8$.

[0033] Moreover, X diffraction measurement by CuK alpha rays was performed about the obtained hydrogen absorption object. Consequently, although peaks, such as KH, were not observed in the field of $x < 8$, the sharp diffraction line appeared $2\theta = 22$ degree and near 32 degree. Moreover, when differential heat scan analysis was performed about the obtained hydrogen absorption object, the exothermic peak accompanying fusion of K was not observed in the field of $x < 8$, either. Furthermore, the hydrogen absorption objects with which the peak of the hydrogen desorption by inert gas conveyance heating-thermal conductimetry was acquired by this example to KH being 540 degrees C were 400 degrees C and 900 degrees C.

[0034] If the above result contacts in hydrogen the reactant set to superfluous K from mixture with a graphite lamellar compound KC8, superfluous K will be incorporated between the layers of a graphite with hydrogen, and it will be thought that forming the intercalation compound of 3 yuan is shown. The detailed analysis of the peak acquired by the X diffraction showed that this 3 yuan intercalation compound was a new compound expressed with empirical formula KC₄H_{0.8}.

[0035] (Example 3) The hydrogen gas occluded substance which consists of graphitized carbon (MCMB 25-28) and Li was produced using the mechanical alloying method. That is, all over the argon permutation dry box (dew-point: -80 degrees C), weighing capacity of graphitized carbon and the Li was carried out at a rate of 3:1 by the mole ratio, and this was put into the mill pot made from stainless steel. Subsequently, milling was carried out by grinding acceleration 10.7G with the planet ball mill for 12 hours.

[0036] This pot was connected to the automatic PCT property measuring device (Made in the Suzuki Trading house), and the hydrogen storage capacity was measured.

Consequently, 0.81wt% occlusion has been checked under a room temperature and the conditions of hydrogen pressure 1.30MPa. Moreover, when X diffraction measurement by CuK alpha rays was performed about the obtained hydrogen absorption object, peaks, such as LiH, were not observed only by a broadcloth diffraction line being observed at one low angle side. Moreover, the hydrogen reactants from which the peak of the hydrogen desorption by inert gas conveyance heating-thermal conductimetry was acquired by this example to LiH being 1000 degrees C were 250 degrees C and 640 degrees C.

[0037] (Example 4) The hydrogen gas occluded substance which consists of graphitized carbon (MCMB 25-28) and K was produced using the mechanical alloying method. That is, all over the argon permutation dry box (dew-point: -80 degrees C), weighing capacity of graphitized carbon and the K was carried out at a rate of 4:1 by the mole ratio, and this was put into the mill pot made from stainless steel. Subsequently, milling was carried out by grinding acceleration 10.7G with the planet ball mill for 12 hours.

[0038] This pot was connected to the automatic PCT property measuring device (Made in the Suzuki Trading house), and the hydrogen storage capacity was measured.

Consequently, 0.81wt% occlusion has been checked under a room temperature and the conditions of hydrogen pressure 1.30MPa. Moreover, when X diffraction measurement by CuK alpha rays was performed about the obtained hydrogen absorption object, peaks, such as KH, were not observed only by a broadcloth diffraction line being observed at one low angle side. Moreover, the hydrogen absorption objects with which the peak of the hydrogen desorption by inert gas conveyance heating-thermal conductimetry was acquired by this example to KH being 540 degrees C were 400 degrees C and 640 degrees C.

[0039] As mentioned above, although the gestalt of operation of this invention was explained to the detail, various alterations are possible for this invention without not being limited to the gestalt of the above-mentioned implementation at all and deviating from the summary of this invention.

[0040] For example, although the above-mentioned example explained the example to which a single alkali metal was made to react to activated carbon or graphitized carbon, two or more sorts of alkali metal may be made to react to activated carbon or graphitized carbon. Moreover, alkali metal may be made to react to this, using the mixture of amorphous ingredients, such as activated carbon, and a graphite as a carbon material.

[0041]

[Effect of the Invention] The hydrogen gas occluded substance concerning this invention consists of a reactant of amorphous carbon and alkali metal, and is effective in the ability to store a lot of hydrogen gas easily in near a room temperature, since the mole ratio of said amorphous carbon to said alkali metal is 26 or less [1.3 or more].

[0042] Moreover, the 2nd of this invention consists of a reactant of a graphite and alkali metal, and they are effective in the ability to store a lot of hydrogen gas easily in near a room temperature, since the mole ratio of said graphite to said alkali metal is less than [2.7 or more] eight.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the mole ratio x of activated carbon and the relation of a hydrogen storage capacity to a potassium.

[Drawing 2] It is drawing showing the mole ratio x of graphitized carbon and the relation of a hydrogen storage capacity to a potassium.

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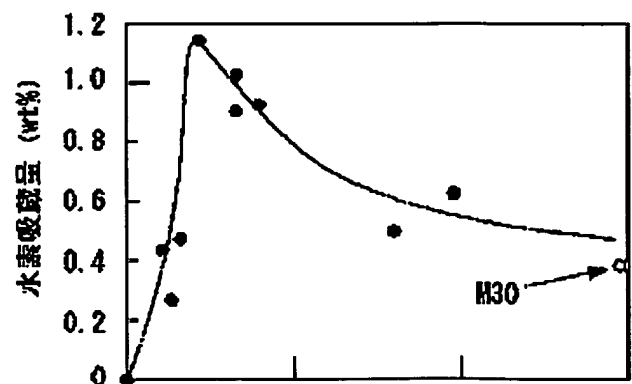
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(54) 【発明の名称】 水素ガス吸蔵物質

(57) 【要約】

【課題】 水素吸蔵量が多く、しかも、室温付近で水素を容易に貯蔵し得る水素ガス吸蔵物質を提供すること。

【解決手段】 本発明に係る水素ガス吸蔵物質は、アルカリ金属と炭素材料の反応物からなる。炭素材料が非晶質炭素である場合には、アルカリ金属に対する非晶質炭素のモル比は、1.3以上2.6以下が好ましい。また、炭素材料が黒鉛である場合には、アルカリ金属に対する黒鉛のモル比は、2.7以上8未満が好ましい。



(2)

特開2002-28483

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【特許請求の範囲】

【請求項1】 非晶質炭素とアルカリ金属との反応物からなり、
前記アルカリ金属に対する前記非晶質炭素のモル比が、
1.3以上2.6以下であることを特徴とする水素ガス吸蔵物質。

【請求項2】 前記非晶質炭素は、高分子化合物、天然高分子及び石油もしくは石炭から得られる生コークスより選ばれる1種もしくは2種以上の材料を500℃以上の温度で熱処理することにより得られたもの、活性炭、又はカーボンファイバーのいずれか1以上である請求項1に記載の水素ガス吸蔵物質。

【請求項3】 黒鉛とアルカリ金属との反応物からなり、

前記アルカリ金属に対する前記黒鉛のモル比が、2.7以上8未満であることを特徴とする水素ガス吸蔵物質。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、水素ガス吸蔵物質に関し、更に詳しくは、非晶質炭素、黒鉛などの炭素材料とアルカリ金属との反応物からなる水素ガス吸蔵物質に関する。

【0002】

【従来の技術】黒鉛結晶は、多種類の原子、分子、イオンなどの化学種（インターカラント）を層間に取り込み、層間化合物を作ることが知られている。黒鉛層間化合物は、使用するインターカラント又は合成条件によって、黒鉛層に対するインターカラント層の周期性（ステージ構造）と、インターカラント層内の構造が大きく変化し、外観、性質の全く異なる化合物が得られるという特徴がある。

【0003】特に、アルカリ金属をインターカラントとして取り込んだ黒鉛層間化合物は、特定の条件下で水素と反応させると、アルカリ金属-黒鉛-水素の三元層間化合物を生成し、生成した三元層間化合物を所定の温度に加熱すると、水素を放出して元のアルカリ金属-黒鉛層間化合物に戻るという性質を示す。そのため、アルカリ金属-黒鉛層間化合物は、水素ガス貯蔵手段、あるいは、水素ガス濃縮手段への応用が期待されているものである。

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Ca 、 H_2 及び CsC_2A 、 H_2 の組成で表される三元層間化合物を形成する。

【0005】

【発明が解決しようとする課題】 KC 、及び RbC に代表される高温型のアルカリ金属-黒鉛層間化合物は、水素の吸蔵を室温近傍で行うことができるので、取り扱いが容易であるという利点がある。しかしながら、 KC 、及び RbC の水素吸蔵量（三元層間化合物の重量に対する吸蔵水素の重量の割合）は、それぞれ、0.50 wt%及び0.028 wt%であり、 LaNi_5 に代表される水素吸蔵合金に比して、水素吸蔵量が少ないという問題がある。

【0006】これに対し、 $\text{KC}_{2.4}$ 、 $\text{RbC}_{2.4}$ 、及び $\text{CsC}_{2.4}$ に代表される低温型のアルカリ金属-黒鉛層間化合物は、高温型のアルカリ金属-黒鉛層間化合物に比して水素吸蔵量が多いという利点がある。特に、 $\text{KC}_{2.4}$ の水素吸蔵量は、水素吸蔵合金とほぼ同等の値を持つ。しかしながら、低温型のアルカリ金属-黒鉛層間化合物は、水素の吸蔵を液体窒素温度付近で行わなければならないので、実用性に乏しいという欠点がある。

【0007】本発明が解決しようとする課題は、水素吸蔵量が多く、しかも、室温付近で水素を容易に貯蔵し得る水素ガス吸蔵物質を提供することにある。

【0008】

【課題を解決するための手段】上記課題を解決するために本発明に係る水素ガス吸蔵物質は、非晶質炭素とアルカリ金属との反応物からなり、前記アルカリ金属に対する前記非晶質炭素のモル比が、1.3以上2.6以下であることを要旨とするものである。

【0009】非晶質炭素とアルカリ金属とを反応させると、アルカリ金属の少なくとも一部が非晶質炭素にドーピングされた反応物得られる。これを室温において水素と接触させると、水素ガスは、非晶質炭素の表面だけでなく、非晶質炭素を構成する結晶子の隙間や結晶子の層間にも吸蔵される。そのため、非晶質炭素単独の場合に比して、水素吸蔵量が増加する。

【0010】また、本発明に係る2番目の水素ガス吸蔵物質は、黒鉛とアルカリ金属との反応物からなり、前記アルカリ金属に対する前記黒鉛のモル比が、2.7以上8未満であることを要旨とするものである。

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【発明の実施の形態】以下、本発明の一実施の形態について詳細に説明する。本発明に係る水素ガス吸蔵物質は、炭素材料とアルカリ金属との反応物からなり、その組成は、組成式 MC_x で表すことができる。但し、組成式中、「M」及び「C」は、それぞれアルカリ金属及び炭素材料を表し、「x」は、アルカリ金属Mに対する炭素材料Cのモル比を表す。

【0013】ここで、アルカリ金属Mは、特に限定されるものではないが、Li、Na、K、Rb、及びCsから選ばれる1種又は2種以上の元素が好ましい。また、これらのアルカリ金属Mは、そのすべてが炭素材料と反応している必要はなく、少なくとも一部が炭素材料と反応していれば良い。

【0014】炭素材料Cには、非晶質炭素又は黒鉛のいずれを用いても良く、特に限定されるものではない。但し、炭素材料Cとして非晶質炭素を用いる場合には、モル比xは、1.3以上2.6以下が好ましい。炭素材料Cが非晶質炭素である場合において、モル比xが1.3未満になると、水素吸蔵に寄与しないアルカリ金属の割合が増加し、水素吸蔵量を低下させるので好ましくない。また、モル比xが2.6を超えると、高い水素吸蔵能を示すアルカリ金属と非晶質炭素の反応物の割合が少なくなり、水素吸蔵量を低下させるので好ましくない。

【0015】また、非晶質炭素としては、具体的には、高分子化合物、天然高分子、及び、石油又は石炭から得られるコークスより選ばれる1種又は2種以上の材料を500℃以上の温度で熱処理することにより得られたものを用いるのが好ましい。この場合、熱処理は、不活性雰囲気下で行うのが好ましい。また、非晶質炭素には、活性炭、カーボンファイバー等を用いても良い。さらに、非晶質炭素は、これらの材料を単独で用いても良く、あるいは、これらの内の2種以上を組み合わせて用いても良い。

【0016】一方、炭素材料Cとして黒鉛を用いる場合には、モル比xは、2.7以上8未満が好ましい。モル比xが2.7未満になると、水素吸蔵に寄与しないアルカリ金属の割合が増加し、水素吸蔵量を低下させるので好ましくない。また、モル比xが8以上になると、水素吸蔵作用を示す高温型のアルカリ金属-黒鉛層間化合物の割合が少なくなり、水素吸蔵量が低下するので好まし

かしながら、この非晶質炭素とアルカリ金属とを反応させて得られる反応物は、非晶質炭素単独の場合に比して水素吸蔵量が大幅に増加する。

【0019】これは、反応によってアルカリ金属の少なくとも一部が非晶質炭素にドーブされるが、ドーブされたアルカリ金属が水素吸蔵の際の触媒として作用し、水素ガスが、非晶質炭素の表面のみならず、非晶質炭素の結晶子の隙間、あるいは結晶子の層間にも吸蔵されるためと考えられる。

【0020】また、室温近傍において水素を吸蔵する作用を示すアルカリ金属-黒鉛層間化合物としては、組成式 MC で表される高温型の黒鉛層間化合物が知られている。従って、炭素材料として黒鉛を用いる場合において、アルカリ金属に対する黒鉛のモル比が2.7以上8未満となるように、黒鉛とアルカリ金属とを反応させると、従来知られている高温型の黒鉛層間化合物と過剰のアルカリ金属からなる混合物が得られる。

【0021】しかしながら、このような反応物と水素とを反応させると、その水素吸蔵量は、反応物中に含まれる高温型黒鉛層間化合物の量から予想される水素吸蔵量よりも多くなる。これは、高温型黒鉛層間化合物と過剰のアルカリ金属からなる混合物と水素とを接触させると、過剰のアルカリ金属が水素と共に黒鉛の層間に取り込まれ、新規な組成を有するアルカリ金属-黒鉛-水素の三元黒鉛層間化合物が生成するためと考えられる。

【0022】次に、本発明に係る水素ガス吸蔵物質の製造方法について説明する。本発明に係る水素ガス吸蔵物質は、種々の方法により製造することができる。例えば、アルカリ金属と炭素材料とを混合し、これを適当な密閉容器に真空封入した後、所定温度に所定時間加熱する方法により製造することができる。また、例えば、アルカリ金属粉末と炭素材料とをボールミルに入れ、強制攪拌するメカニカルアロイング法によっても製造することができる。

【0023】

【実施例】（実施例1）炭素材料及びアルカリ金属として、それぞれ、活性炭（M30、大阪ガスケミカル（株）製）及びKを用い、Kに対する活性炭のモル比xが、それぞれ、0、1.09、1.33、1.63、2.17、3.26、4.8、及び9.77となるよう

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続し、サンプルセル管内部を0.13Paまで真空引きした後、ジョイントを取り外した。その後、サンプルセル管を電気炉中に300℃で22時間放置し、Kと活性炭の反応物を得た。

【0026】得られた反応物について、それぞれ、X線回折測定を行った。その結果、 $x < 8$ である場合、反応物は、Kと、Kがドーブされた活性炭の混合物であることがわかった。また、 $x \geq 8$ である場合、反応物は、Kがドーブされた活性炭のみからなることがわかった。X線回折パターンにおいて、活性炭特有の小角散乱は見られなかったことから、Kは、活性炭表面の細孔内に充填されているものと考えられる。

【0027】次に、反応物が封入されたサンプルセル管を自動P T C特性測定装置に取り付け、室温において水素圧4.95MPaの条件下で水素を吸蔵させた。水素を吸蔵させた反応物（以下、これを「水素吸蔵物」という。）のモル比 x と、水素吸蔵量との関係を図1に示す。なお、図1には、活性炭(M30)の水素吸蔵量も併せて示した。図1より、モル比 x が、 $1.3 \leq x \leq 2.6$ の範囲内において、水素吸蔵物の水素吸蔵量が、従来から知られているKC、 H_2 、より多くなっていることがわかる。

【0028】また、得られた水素吸蔵物について、それぞれ、X線回折測定を行った。その結果、Kを過剰に加えた $x < 8$ の領域であっても、KH等のピークは観察されず、水素吸蔵物に起因するブロードな回折ピークのみが観察された。また、不活性ガス搬送加熱-熱伝導度法により水素放出のピークを測定したところ、KHは540℃であるのに対し、本実施例で得られた水素吸蔵物は、400℃と900℃であった。

【0029】以上の結果は、過剰のKを含む反応物と水素ガスとを接触させると、過剰のKが水素と共に活性炭の内部（例えば、結晶子の隙間、結晶子の層間など。）に入り込むことを示していると考えられる。

【0030】（実施例2）炭素材料及びアルカリ金属として、それぞれ、黒鉛化炭素(MCMB25-28)及びKを用い、Kに対する黒鉛化炭素のモル比 x が、それぞれ、0、1.09、2.17、3.26、4.5、43.7、89.8、13.02、及び ∞ （すなわち、黒鉛化炭素のみ。）となるように秤量した以外は、実施例

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を自動P T C特性測定装置に取り付け、室温において水素圧4.95MPaの条件下で水素を吸蔵させた。得られた水素吸蔵物のモル比 x と、水素吸蔵量との関係を図2に示す。なお、図2には、黒鉛化炭素(MCMB25-28)の水素吸蔵量も併せて示した。図2より、モル比 x が、 $2.7 \leq x < 8$ の範囲内において、水素吸蔵物の水素吸蔵量が、従来から知られているKC、 H_2 、より多くなっていることがわかる。

【0033】また、得られた水素吸蔵物について、Cu K α 線によるX線回折測定を行った。その結果、 $x < 8$ の領域においてもKH等のピークは観察されなかったが、鋭い回折線が $2\theta = 22^\circ$ 、 32° 付近に現れた。また、得られた水素吸蔵物について示差熱分析を行ったところ、 $x < 8$ の領域でも、Kの融解に伴う発熱ピークは観察されなかった。さらに、不活性ガス搬送加熱-熱伝導法による水素放出のピークは、KHが540℃であるのに対し、本実施例で得られた水素吸蔵物は、400℃と900℃であった。

【0034】以上の結果は、過剰のKと、黒鉛層間化合物KC、との混合物からなる反応物を水素と接触させると、過剰なKが水素と共に黒鉛の層間に取り込まれ、三元層間化合物を形成することを示していると考えられる。X線回折で得られたピークの詳細な解析により、この三元層間化合物が、組成式KC $_x$ H $_y$ で表される新規な化合物であることがわかった。

【0035】（実施例3）メカニカルアロイング法を用いて、黒鉛化炭素(MCMB25-28)とLiからなる水素ガス吸蔵物質を作製した。すなわち、アルゴン置換ドライボックス（露点：-80℃）中で、黒鉛化炭素とLiとをモル比で3：1の割合で秤量し、これをステンレス製ミルポットに入れた。次いで、遊星ボールミルで粉碎加速度10.7Gで12時間ミリングした。

【0036】このポットを自動PCT特性測定装置（（株）鈴木商館製）に接続し、水素吸蔵量の測定を行った。その結果、室温、水素圧1.30MPaの条件下で、0.81wt%の吸蔵を確認できた。また、得られた水素吸蔵物について、Cu K α 線によるX線回折測定を行ったところ、ブロードな回折線が低角側に1つ観察されるだけで、LiH等のピークは観察されなかった。また、不活性ガス搬送加熱-熱伝導法による水素放出の

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【0038】このポットを自動PCT特性測定装置（（株）鈴木商船製）に接続し、水素吸蔵量の測定を行った。その結果、室温、水素圧1.30MPaの条件下で、0.81wt%の吸蔵を確認できた。また、得られた水素吸蔵物について、CuK α 線によるX線回折測定を行ったところ、ブロードな回折線が低角側に1つ観察されるだけで、KH等のピークは観察されなかった。また、不活性ガス搬送加熱-熱伝導法による水素放出のピークは、KHが540℃であるのに対し、本実施例で得られた水素吸蔵物は、400℃と640℃であった。

【0039】以上、本発明の実施の形態について詳細に説明したが、本発明は上記実施の形態に何ら限定されるものではなく、本発明の要旨を逸脱しないで種々の改変が可能である。

【0040】例えば、上記実施例では、活性炭又は黒鉛化炭素に対して、単一のアルカリ金属を反応させた例について説明したが、活性炭又は黒鉛化炭素に対して、2種以上のアルカリ金属を反応させても良い。また、活性*

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*炭等の非晶質材料と黒鉛との混合物を炭素材料として用い、これに対してアルカリ金属を反応させても良い。

【0041】

【発明の効果】本発明に係る水素ガス吸蔵物質は、非晶質炭素とアルカリ金属との反応物からなり、前記アルカリ金属に対する前記非晶質炭素のモル比が、1.3以上2.6以下であるので、室温付近において、多量の水素ガスを容易に貯蔵できるという効果がある。

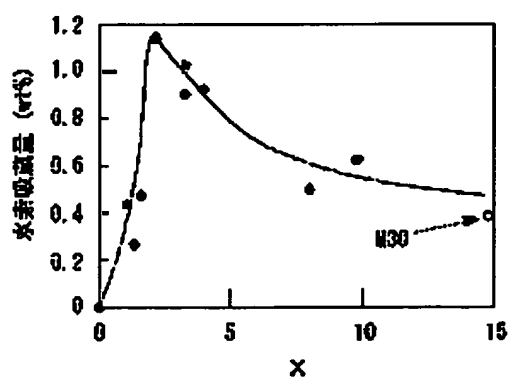
【0042】また、本発明の2番目は、黒鉛とアルカリ金属との反応物からなり、前記アルカリ金属に対する前記黒鉛のモル比が、2.7以上8未満であるので、室温付近において、多量の水素ガスを容易に貯蔵できるという効果がある。

【図面の簡単な説明】

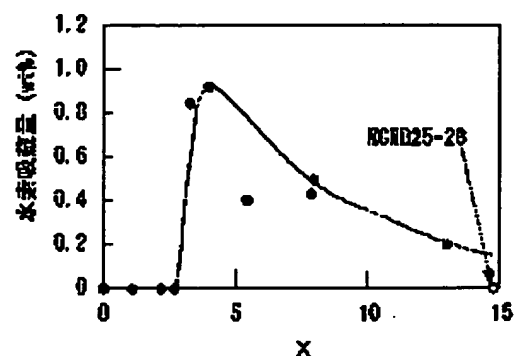
【図1】 カリウムに対する活性炭のモル比xと水素吸蔵量の関係を示す図である。

【図2】 カリウムに対する黒鉛化炭素のモル比xと水素吸蔵量の関係を示す図である。

【図1】



【図2】



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